

value between 1.0 and 2.4 eV, thus making it possible to fabricate cells containing high and/or graded bandgaps.

A "single-source precursor compound" is a single molecular compound that contains all the required elements, which when used under the spray CVD conditions, thermally decomposes to form  $\text{CuIn}_x\text{Ga}_{1-x}\text{S}_y\text{Se}_{2-y}$ . Relative to the use of multiple precursor reagents, the use of single-source precursors offers the advantage of better regulation of the chemical composition of the deposit, less susceptibility to contamination, and, most importantly, a simplified fabrication process.

The improved single-source precursor compounds of the invention are denoted by the general formula

$[(\text{LR}_3)_2\text{Cu}(\text{ER}')_2\text{M}(\text{ER}')_2]$ , where L signifies P, As, or Sb; R or R' signifies an alkyl or aryl group; and E signifies S or Se. The general formula and molecular structure afford flexibility for tailoring the precursor to suit a specific CVD spray process and to tailor the chemical composition (more specifically, the proportions  $x$  and  $y$ ) of  $\text{CuIn}_x\text{Ga}_{1-x}\text{S}_y\text{Se}_{2-y}$  formed in the process. In addition, by choosing L, R, R', and E according to their steric and electronic properties, one can tailor decomposition temperatures and the phases in the deposit.

A single-source precursor of the invention can be synthesized by the reaction of a stabilized Cu(I) cation with an In(III) or Ga(III) chalcogenide anion prepared *in situ* by reaction of the conju-

gate acid of the thiol or selenol with NaOEt (where Et signifies an ethyl group) in  $\text{CH}_3\text{OH}$ , as in the example of the figure. Alternatively, one could synthesize a single-source precursor by use of commercially available reagents in a new facile one-pot process: For example one could react  $\text{NaSCH}_3$  with  $\text{InCl}_3$  and add CuCl and  $\text{PR}_3$ .

*This work was done by Kulbinder K. Banger, Jerry Harris, and Aloysius Hepp of Glenn Research Center. Further information is contained in a TSP (see page 1).*

*Inquiries concerning rights for the commercial use of this invention should be addressed to NASA Glenn Research Center, Innovative Partnerships Office, Attn: Steve Fedor, Mail Stop 4-8, 21000 Brookpark Road, Cleveland, Ohio 44135. Refer to LEW-17445-1.*

## Spray CVD for Making Solar-Cell Absorber Layers

**Spray CVD combines the advantages of metalorganic CVD and spray pyrolysis.**

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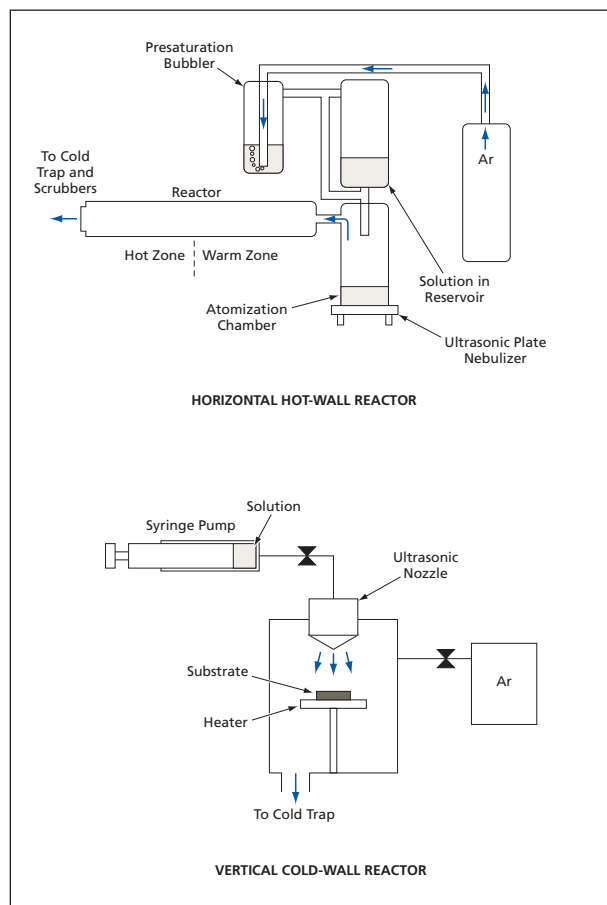
Spray chemical vapor deposition (spray CVD) processes of a special type have been investigated for use in making  $\text{CuInS}_2$  absorber layers of thin-film solar photovoltaic cells from either of two subclasses of precursor compounds:  $[(\text{PBu}_3)_2\text{Cu}(\text{SEt})_2\text{In}(\text{SEt})_2]$  or  $[(\text{PPh}_3)_2\text{Cu}(\text{SEt})_2\text{In}(\text{SEt})_2]$  {where Bu, Et, and Ph signify butyl, ethyl, and phenyl groups, respectively}.  $\text{CuInS}_2$  is a member of the class of chalcopyrite semiconductors described in the immediately preceding article.  $[(\text{PBu}_3)_2\text{Cu}(\text{SEt})_2\text{In}(\text{SEt})_2]$  and  $[(\text{PPh}_3)_2\text{Cu}(\text{SEt})_2\text{In}(\text{SEt})_2]$  are members of the class of single-source precursors also described in the preceding article.

In a spray CVD process of this type, a room-temperature solution containing the precursor compound is first ultrasonically nebulized. The resulting aerosol is swept into a two-zone reactor by a flow of argon, which serves as a nonreactive carrier gas. In the reactor, the aerosol first encounters the evaporation zone, which is a warm zone wherein the solvent and precursor evaporate. The resulting mixture of gases then enters the deposition zone, which is a hot zone wherein the precursor decomposes and the semiconductor film grows on a substrate as in conventional CVD.

Spray CVD affords a combination of the most desirable features (but without

the major difficulties) of metalorganic CVD and spray pyrolysis. These desirable features include growth of the film in an inert atmosphere, capability for deposition on a large area, laminar flow over the substrate, and storage and delivery of the precursor from a cool solution reservoir. The last-mentioned feature is especially advantageous in that it can prevent premature decomposition of a thermally labile precursor.

Two different spray CVD processes of this type have been tested in experiments thus far. In one process, a horizontal hot-wall reactor was used; in the other process, a vertical cold-wall reactor was used (see figure). In each process, the flow rate of argon was typically about 4 L/min. For the horizontal hot-wall re-



A Horizontal Hot-Wall and a Vertical Cold-Wall Reactor have been used in experiments on spray CVD for deposition of thin  $\text{CuInS}_2$  films.

actor, the aerosol was generated by use of an ultrasonic plate nebulizer excited at a frequency of 2.5 MHz; for the vertical-cold-wall reactor, a syringe pump delivered the solution at a rate of 1.5 mL/min to the nebulizer, wherein the aerosol was generated by use of an atomizing ultrasonic nozzle excited at a frequency of 120 kHz. In the horizontal hot-wall reactor, the portion of the wall in the evaporation zone was heated to a temperature of 130 °C, while the portion of the wall in the deposition zone was

heated to about 400 °C. In the vertical cold-wall reactor, as its name suggests, the wall was not heated; instead, the substrate was heated to 400 °C.

The CuInS<sub>2</sub> films produced in the experiments have been characterized by x-ray diffraction, scanning electron microscopy, energy-dispersive spectroscopy, and four-point-probe electrical tests. The results of these tests have provided some guidance for refinement of the spray CVD processes and for annealing and possibly other post-process steps to im-

prove the quality of the deposited CuInS<sub>2</sub> films.

*This work was done by Kulbinder K. Banger, Jerry Harris, Michael H. Jin, and Aloysius Hepp of Glenn Research Center. Further information is contained in a TSP (see page 1).*

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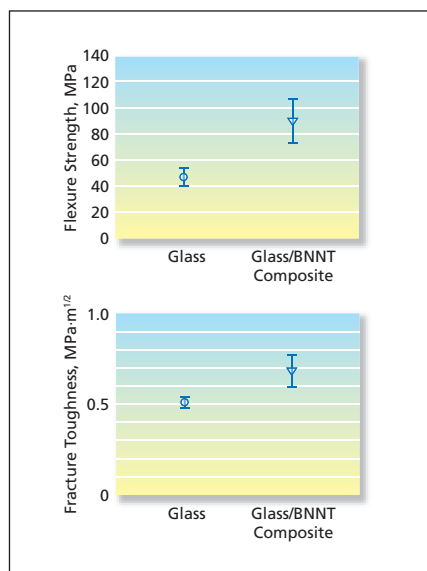
## Glass/BNNT Composite for Sealing Solid Oxide Fuel Cells

**Boron nitride nanotubes contribute to strength and fracture toughness.**

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A material consisting of a barium calcium aluminosilicate glass reinforced with 4 weight percent of boron nitride nanotubes (BNNTs) has shown promise for use as a sealant in planar solid oxide fuel cells (SOFCs). The composition of the glass in question in mole percentages is 35BaO + 15CaO + 5Al<sub>2</sub>O<sub>3</sub> + 10B<sub>2</sub>O<sub>3</sub> + 35SiO<sub>2</sub>. The glass was formulated to have physical and chemical properties suitable for use as a planar-SOFC sealant, but has been found to be deficient in one aspect: it is susceptible to cracking during thermal cycling of the fuel cells. The goal in formulating the glass/BNNT composite material was to (1) retain the physical and chemical advantages that led to the prior selection of the barium calcium aluminosilicate glass as the sealant while (2) increasing strength and fracture toughness so as to reduce the tendency toward cracking.

In preparation for tests, panels of the glass/BNNT composite were hot pressed and machined into test bars. Properties of the test bars, including four-point flexure strength, modulus of elasticity, mi-



**Flexure Strength and Fracture Toughness** of the glass and the glass/BNNT composite are compared here, with error bars signifying one standard deviation.

crohardness, and density were determined. In addition, fracture toughness was measured by the single-edge V-notch-beam method. Among the conclu-

sions drawn from the results of the tests were that the flexure strength and fracture toughness of the glass/BNNT composite specimens were greater than those of neat glass specimens by amounts of about 90 percent and about 35 percent, respectively (see figure). It was further concluded that these increases would greatly prolong the lifetimes of SOFC seals, yet there would be little adverse effect on sealing behavior of the glass because the relatively small concentration of BNNTs needed to obtain these increases would not cause much change in the viscosity of the composite sealant material.

*This work was done by Narottam P. Bansal and Janet B. Hurst of Glenn Research Center and Sung R. Choi of the University of Toledo. Further information is contained in a TSP (see page 1).*

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